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A STATUS REVIEW OF LEWIS RESEARCH CENTER SUPPORTED PROTECTION SYSTEM DEVELOPMENT

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ABSTRACT

The status of several Lewis Research Center sponsored coating research and development studies is reviewed. Efforts on protecting superalloy and dispersion strengthened materials for aircraft gas turbine engines and on protecting refractory metals for re-entry systems are discussed.

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SUMMARY

Lewis Research Center sponsored coating development for superalloys has produced several promising systems including vapor deposited CoCrAlY coatings, alumina enriched aluminide coatings and metallic claddings. Efforts to minimize the interdiffusion of dispersion strengthened materials and protection systems have shown only modest success. Fused slurry silicide coatings for columbium re-entry hardware are being optimized while process development and scale-up are underway. Several promising fused slurry silicide coatings have been developed for tantalum re-entry hardware.

INTRODUCTION

Currently, the Lewis Research Center is supporting a variety of both contractual and in-house coating development and evaluation studies. These include efforts to protect:

(a) Superalloys for aircraft gas turbine engine blade and vane service

(b) Dispersion strengthened nickel materials for turbine vane use

(c) Refractory metals for space shuttle thermal protection systems

(d) Refractory metals for very high temperature turbine vanes, etc.

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(e) Alloy steels for thermal reactors to control automotive exhaust

(f) Stainless steel regeneratively cooled nozzles for hydrogen (nuclear) and hydrogen-oxygen (chemical) rocket engines

(g) Titanium alloy blades for high performance aircraft compressors (RFP issued)

In many of these applications, coatings which were once used only to extend component life are now becoming necessary for successful system operation. For this reason, the Lewis program is directed toward increasing protection system reliability, increasing protective life, and developing a fundamental understanding of these protection systems needed to predict useful life.

The purpose of this paper is to briefly highlight the current development status for coatings in the first three areas listed above.

SUPERALLOY/DISPERSION STRENGTHENED MATERIALS FOR AIRCRAFT GAS TURBINE ENGINES

Three major approaches are being taken to improve protection systems for aircraft gas turbine engines: (1) characterize the protection ability of currently available coatings; (2) develop improved coatings for current alloys; and (3) develop new protection systems for advanced alloys.

Coatings for Superalloys

In Ref. 1, three commercial aluminide coatings on either IN-100, B-1900, WI-52 or X-40 were found to vary considerably in their chemistry, microstructure, and ability to resist jet fueled burner rig oxidation. Since commercial coating vendors do not disclose deposition parameters or treatments, the origins of these differences are not well understood. To provide

a better basis for understanding and to aid in future aluminide coating improvement, an in-house study at Lewis is examining the influence of pack cementation variables on aluminide coatings applied to nickel-base alloy IN-100. Data are being generated on the effects of activators, time, and temperature. In support of this and other efforts to extend coating life, better characterization methods for aluminide coatings are also being sought. Electron microprobe, ion microprobe, metallographic, and X-ray data are being compared to establish just how well total coating characterization can be accomplished.

Two contractual programs have been successful in developing improved coating systems for the high strength nickel superalloy NASA-TRW VIA. A physical vapor deposited CoCrAlY coating has been developed under NAS 3-12415 by Pratt and Whitney Aircraft. In P. &W. burner rig tests of coated, simulated airfoil specimens conducted at 1093° C (2000° F), the best system survived over 1100 hours and still had residual protection capability. Based on a weight loss criteria of time to lose a total of 20 mg, this coating was about three times as protective as a current slurry aluminide coating (now in engine service) also applied to VIA. Figure 1 is a comparison of such weight change behavior (the curves have been smoothed for ease of comparison).

Under NAS 3-11160, the General Electric Company has developed an aluminide coating containing finely divided aluminum oxide by means of a modified pack cementation process. Their low velocity, burner rig tests at 1093° C (2000° F) indicated that this coating had a life greater than 1300 hours (based on time to show a net weight loss) - significantly better than production systems. The results of the two programs cannot be directly compared since no cross correlation exists between the test rigs. However, burner rig tests are being conducted at Lewis Research Center to compare the two systems under the same test conditions.

A third contractual program examined various other coatings

deposited on VIA by fused salt metalliding. Combinations of chromium-manganese (Cr-Mn), chromium-yttrium (Cr-Y), yttrium-zirconium (Y-Zr), and tantalum-aluminum (Ta-Al) were not as protective as straight aluminiding from a fused salt bath (NAS 3-12414, General Electric Company). The final reports on all three of the above programs will be distributed shortly.

Further study of aluminiding from fused salt baths is being conducted under NAS 3-14300 (General Electric - Schnectady). The objectives of this program are to optimize parameters for aluminizing IN-100; to investigate co-deposition of Cr, titanium (Ti), silicon (Si), and one rare earth with aluminum from fused salt metalliding baths; and to determine the feasibility of enriching TD-NiCr (nickel (Ni)-20Cr-2v/o thorium oxide (ThO_2)) with about 5% aluminum so as to form an oxidation resistant NiCrAl matrix. To date, it has been shown that by increasing the current density of the metalliding bath, the driving force for aluminum can be varied so as to produce coatings whose microstructures range in similarity from low activity pack coatings to high activity pack coatings.

Oxidation resistant metallic claddings for superalloys offer an alternative way to impart improved surface protection. Cladding studies on superalloys and dispersion strengthened nickel materials have been under study at Lewis for several years (see ref. 2). The influences of furnace oxidation cycle frequency, cladding thickness, and exposure temperature have been examined for Ni-20Cr-4Al, Ni-30Cr, and iron (Fe) alloy Fe-25Cr-4Al-1Y claddings on IN-100 (nickel base) and WI-52 (cobalt base) superalloys. The results of these tests, as well as those of burner rig tests on clad superalloys are in the final stages of analysis.

Coatings for TD-Ni and TD-NiCr

Mach 1 burner rig test results have been reported (ref. 3) in which 5

mil claddings of NiCrAl and FeCrAlY were applied to TD-NiCr and evaluated at 1149° C (2100° F). Figure 2 shows the relative protection afforded by these claddings. The NiCrAl claddings extend the time before significant oxidation attack (as evidenced by rapid weight losses) by about threefold compared to unprotected TD-NiCr and by about tenfold compared to aluminized WI-52 (ref. 4). The latter is a vane combination used at lower temperatures in present commercial jet engines. Thus, NiCrAl clad TD-NiCr may offer promise for high temperature vane service. The FeCrAlY claddings were less protective and metallographic examination showed that considerable interdiffusion had taken place between the cladding and the TD-NiCr.

Two contractual programs are in progress to minimize such interdiffusion between protection systems for TD-Ni (nickel -2v/oThO_2) and for TD-NiCr and thereby extend their high temperature life under oxidizing conditions. Under NAS 3-14314, the General Electric Company is developing diffusion barriers for aluminide coatings. The G. E. approach involves pack cementation applied chromized/carburized barriers and plasma sparyed X-40, Hastelloy C1 and C2 barriers. These layers are aluminized with the aluminum oxide enriched pack coating discussed previously. Other enriching agents such as molybdenum (Mo)-Al, Cr-Al, and cobalt (Co)-Al compounds are also being evaluated in an effort to provide additional aluminum reservoir capacity and thus extend coating life. Compatibility studies to date indicate that the X-40 is relatively compatible with TD-NiCr while Hastelloy C1 and C2 are compatible with both TD-Ni and TD-NiCr for 100 hours at 1260° C (2300° F). However, tungsten (W), molybdenum (Mo), and other elements do diffuse into the substrate and generally increase substrate hardness.

The second coating/diffusion barrier program for TD-Ni and TD-NiCr is examining barriers to minimize the interdiffusion of oxidation resistant NiCrAl and FeCrAl claddings during high temperature service (NAS 3-14312, Solar Div., International Harvester Company).

Barriers are being examined to minimize diffusion coefficients (YNi_4, $Cr_{23}C_6$, tantalum carbide (TaC), Mo, W); to lower the concentration gradient across the interface by forming intermetallic compounds with aluminum (Ta), etc.; and to reduce the effective area across which diffusion can occur (continuous and discontinuous aluminum oxide-Al_2O_3). For both FeCrAl clad TD-Ni and TD-NiCr none of the barriers had any effect on the rapid interdiffusion of aluminum (the main element responsible for oxidation resistance) during 100 hours at 1260° C (2300° F). Some of the barriers did tend to minimize Al diffusion from NiCrAl. Of the barriers examined, a foil cladding of W appeared the most effective in retaining the Al content of the NiCrAl cladding for both TD-Ni and TD-NiCr as shown in Figure 3. The influences of these low ductility diffusion barriers on mechanical properties and oxidation resistance of the clad systems still remain to be examined.

SILICIDE COATED REFRACTORY METALS FOR SPACE SHUTTLE HEAT SHIELDS

Coating for Columbium

Presently, fused slurry silicide coated columbium alloys are in prominent contention for heat shields of the thermal protection system (TPS) of the space shuttle system in areas which will reach about 1316° C (2400° F). The design goal for these heat shields is a 100 mission life with only minimal refurbishment.

Since considerable prior work has been accomplished under U.S. Air Force support, coated columbium is at a stage of development where coating chemistry, coating processing, and TPS designs can be optimized. Under NAS 3-14307, (McDonnell-Douglas/Sylvania-subcontractor) one of the best coatings - R 512E, Si-20Cr-20Fe - is being applied and evaluated on five candidate columbium alloys: Cb-752, FS-85, C-129Y, B-66 and WC-3015. Oxidation, emittance and mechanical property testing through stress-pressure-temperature re-entry simulation on as-coated and intentionally defected specimens will be supported by fabrication studies

proceeding to full sized heat shield panels. On the basis of these studies, an optimum coating/alloy combination will be identified and evaluated. To date, pre- and post weld ductility data confirm that FS-85, C-129Y, and Cb-752 offer better fabricability. Tensile data on Cb-752 corrected for the loss of .025 to .037 mm (1 to $1\frac{1}{2}$ mils) per side of original specimen cross section due to coating reaction, indicate that the room temperature and elevated temperature tensile strength is not significantly affected by the coating. Also, preliminary McDonnell data indicate that Cb-752 and FS-85 undergo little loss of tensile yield strength above that associated with the further reduction of about $\frac{1}{4}$ mil per side of cross section caused by continued coating interdiffusion during 100 simulated re-entry cycles. On this same program, Sylvania, the original developer of the R 512E coating, is conducting a process optimization and scale up effort to insure that full sized rib-stiffened panels can be uniformly, reliably, and reproducibly coated on a production basis. Various binders, organic vehicles, and slurry additives are being evaluated in order to increase coating green strength and improve handling characteristics; decrease the time to coat a panel; and improve the coating coverage on edges.

Supportive studies are being conducted at Lewis Research Center to provide an independent evaluation of the environmental, mechanical, and compositional characteristics of promising coatings for columbium alloys. In addition to R 512E, the Vac Hyd Corp. VH 109 coating is also being examined as well as any other potentially promising systems. Preliminary oxidation data for these coatings on FS-85 and Cb-752 are presented in Figure 4. This figure shows that these coatings can survive 100 cycles to 1316° C (2400° F) and also have adequate overshoot capability of over 100° C (about 200° F) when exposed in one-half hour cycles in a static 10 torr air environment (a pressure near that expected at maximum heat shield temperature upon re-entry). Each one-half hour cycle is about two to three times as long as the time at 1316° C (2400° F) expected in a shuttle re-entry. While the chemistries of both the coatings on the columbium

alloy Cb-752 are somewhat different, their reduced pressure performance is similar due to the excellent coverage and more than adequate life of 3 mil fused slurry coatings.

The more severe slow cycle tests (right hand column) at ambient pressure did not detect any marked tendency toward rapid intermediate temperature oxidation except in the Si-20titanium (Ti)-10 Mo (R 512C) coated tantalum alloy T-222. The majority of the local coating breakdowns observed on coated columbium were at specimen edges. Breakdown was considered to be the first appearance of a columbium oxide (Cb_2O_5) protrusion. This by no means indicates that a structure developing such an oxide protrusion will fail since the growth rate of the surrounding oxygen contaminated area is moderated by the coating.

Figure 5 shows some preliminary Lewis Research Center tensile data, not corrected for cross sectional losses. However, it is interesting to note that the influence of the R 512E and VH 109 on the properties of Cb752 are similar. Also, R 512E has about the same minimal effects on Cb752 as on FS-85.

Coating for Tantalum

At the time the initial materials were selected for potential TPS use, tantalum was not chosen because no coating was available with 100 mission potential. An effort is now being conducted to develop sufficiently protective coatings so that a better assessment of the utility of coated tantalum can be made.

Two efforts, NAS 3-14315 with Solar and NAS 3-14316 with Lockheed, are about six months into the coating development effort. Initial low pressure tests to about 1427^{o} C (2600^{o} F) indicate that both contractors have achieved improved protection as compared to the R 512C coating (recall the data in Fig. 4). Preliminary test data are presented in Figure 6. This figure shows that lives several times longer than that of R 512C - the only

commercial coating with shuttle potential - have been achieved. However, consistent 100 cycle protection must still be demonstrated and shown to have no attendant degradation on mechanical properties. If the promising results continue, it will be possible to carry over most of the fabrication and panel design technology of columbium to tantalum and thereby extend the useful temperature capabilities of coated refractory metal panels by over one hundred degrees centigrade.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, February 18, 1971

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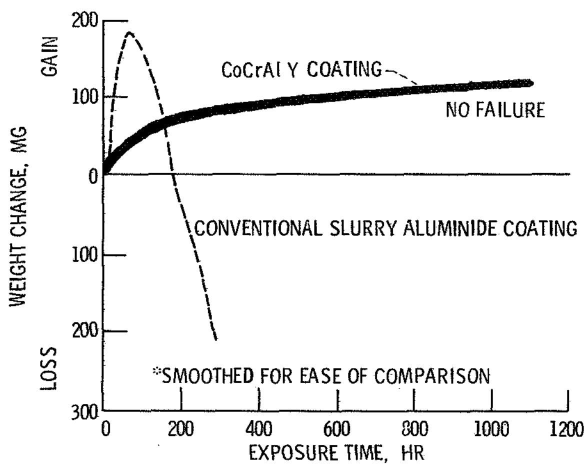


Figure 1. - Comparison of oxidation resistance of advanced and conventional coatings on NASA-TRW nickel alloy VIA. P&W burner rig test data* 1093° C (2000° F) - 1 hour cycles.

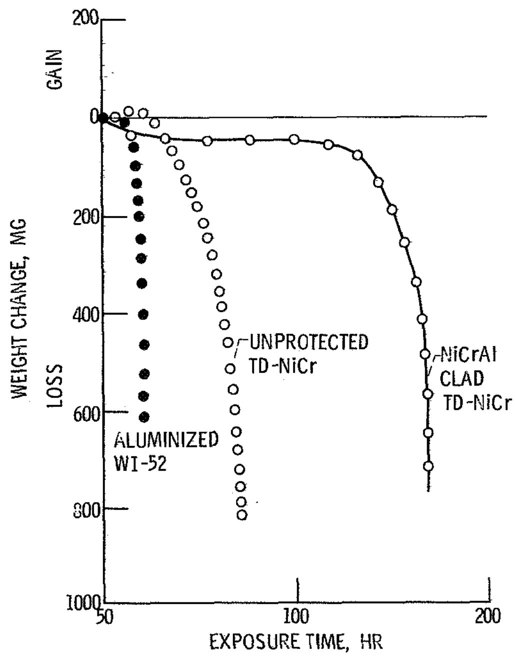


Figure 2. - A 0.125 mm cladding improves the environmental resistance of TD-NiCr at 1140° C. Mach 1 burner rig - 1 hour cycles.

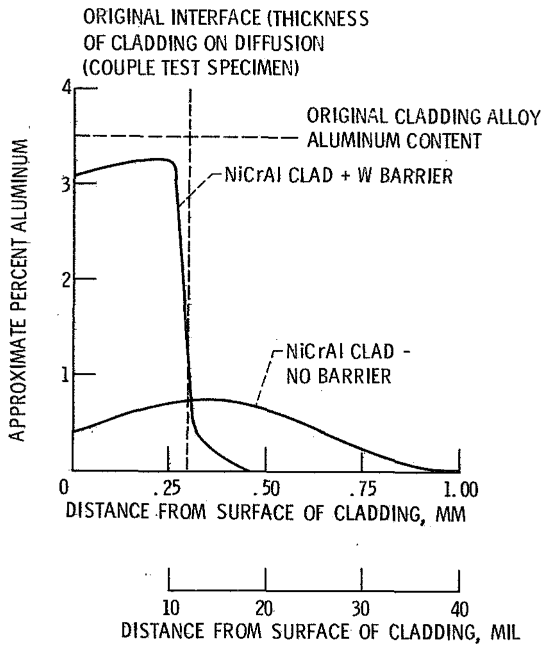
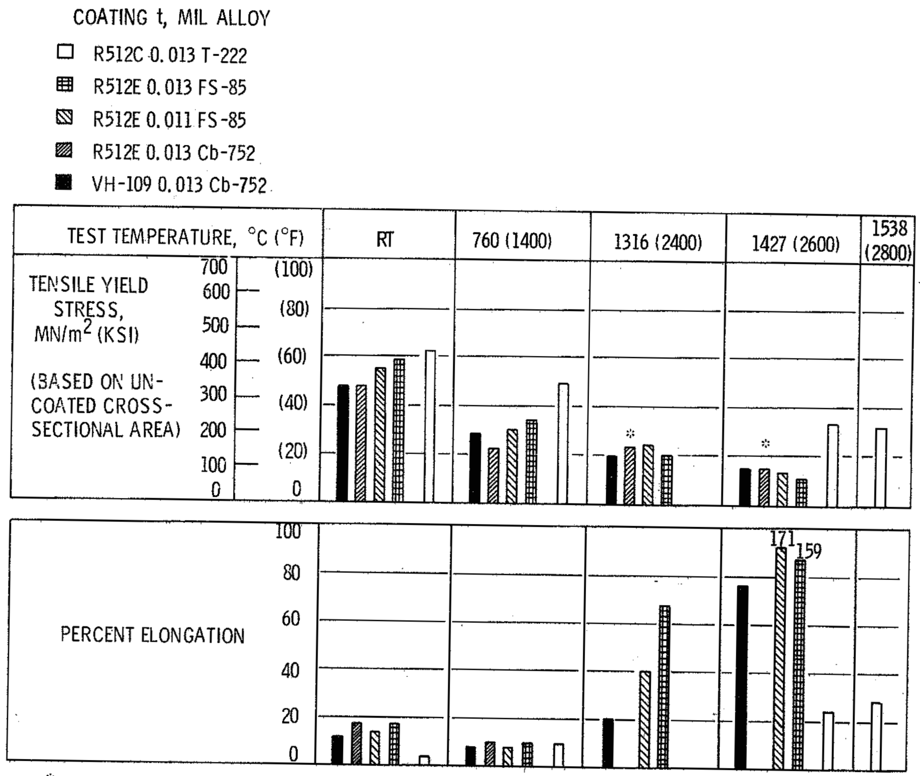


Figure 3. - The aluminum content of NiCrAl clad TD-Ni after annealing for 100 hours in Ar at 1260° C (2300° F).

COATING-ALLOY THICKNESS, ALLOY DESIGNATION	CYCLES TO LOCAL COATING BREAKDOWN					
	10 TORR, CYCLIC SELF-RESISTANCE HEATING 1/2 HOUR AT MAXIMUM TEMPERATURE					AMBIENT PRESSURE, SLOW CYCLE, TUBE FURNACE, 1371 (2500)
	T° C (°F), OPTICAL 1224 (2235) T° C (°F), (ϵ_λ = 0.85) 1240 (2265)	1279 (2335) 1299 (2370)	1335 (2435) 1354 (2470)	1391 (2535) 1410 (2570)	1446 (2635) 1466 (2670)	
VH109 - 13 MIL, Cb752	----	>100	----	>100	-----	21, 21
R 512E - 13 MIL, Cb752	----	>100	----	>100	-----	34, 67
Si-Cr-Fe* - 13 MIL, Cb752	>100	----	>100	----	15, 18	-----
R512E - 11 MIL, FS-85	----	>100	----	>100	-----	42, 42
R512E - 13 MIL, FS-85	----	>100	----	>100	-----	34, 34
Si-Cr-Fe* - 13 MIL, FS-85	>100	----	>100	----	59	37, 37, 37, >38
Si-Cr-Fe* - 10 MIL, FS-85	>100, 31	----	----	----	-----	-----
R512C - 13 MIL, T-222	-------	82	----	14	-----	13, 13, 15, 15

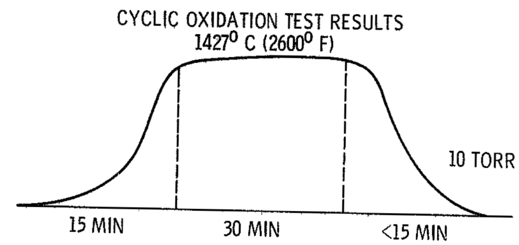
*Si-20Cr-20Fe APPLIED AT LEWIS RESEARCH CENTER

Figure 4. - Oxidation test results on coated refractory metals; preliminary data.



*T. C. REACTED WITH COATING.

Figure 5. - Mechanical property tests results on as-coated columbium alloys and tantalum alloy T-222.



	COATING		CYCLES TO FIRST VISUAL LOCAL COATING BREAKDOWN
	SOLAR-NAS 3-14315		
SINGLE COATING	Si-20Ti-10Mo		10
	Si-4Mo-4W-10Ti-2V-20Cr		43
	Si-10Mo-5Ti-5V-20FE		100+
DUPLEX COATING	FE-20Mo-15W-3Ti-3V	Si-20FE	40
	FE-40Mo-3Ti-3V	Si-20FE	43*
	FE-30Mo-10W-3Ti-3V	Si-20FE	45*
	FE-20Mo-10W-6Ti-6V	Si-20FE	57*
*INTENTIONALLY DEFECTED BY REMOVING A 0.030 IN. DIAM. SPOT			
	LOCKHEED-NAS 3-14316		
SINGLE COATING	Si-33Co-22Mo		59, 84, 100+
	Si-20MN-27Ti		50, 84-100, 100+
	Si-20Ti-10Mo		8-10

Figure 6. - Progress in protection systems for tantalum alloy Ta-10W.